CPP 38: Modeling and Simulation of Soft Matter II (joint session CPP/DY)

Time: Wednesday 9:30–12:00   Location: C 230

Invited Talk   CPP 38.1   Wed 9:30   C 230
The favorite polymer libations — •Carlos M. Marques[1], Debashish Mukherji[2], and Kurt Kremer[2] — [1]Institut Charles Sadron, UdS-CNRS, Strasbourg, France — [2]Max-Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz Germany

Macromolecular solubility in solvent mixtures often strikes as a paradoxical phenomenon. In a system where all particle interactions are repulsive, chains can nevertheless collapse. And when attractive interactions settle in, they might collapse or swell the chain. We will review in this contribution how the puzzling behavior of polymers in aqueous alcohol solutions triggered a better understanding of the interplay between solvent composition and polymer conformation. And how the resulting view on polymer collapse and swelling takes us well beyond mean-field descriptions ... and alcohol.

[1] Mukherji, D., Marques, C. M., Kremer, K. (2014). Polymer collapse in miscible good solvents is a generic phenomenon driven by preferential adsorption. Nature communications, 5882, 5.

[2] Mukherji, D., Marques, C. M., Stuehn, T., Kremer, K. (2015). Co-non-solvency: Mean-field polymer theory does not describe polymer collapse transition in a mixture of two competing good solvents. The Journal of chemical physics, 142(11), 114903.

[3] Mukherji, D., Wagner, M., Watson, M. D., Winzen, S., de Oliveira, T. E., Marques, C. M., & Kremer, K. (2016). Relating side chain organization of PNIPAm with its conformation in aqueous methanol. Soft Matter, 12(38), 7995.

[4] Mukherji, D., Marques, C. M., Stuehn, T., Kremer, K. (2017). Depleted depletion drives polymer swelling in poor solvent mixtures. Nature communications, 1374, 8.

[5] Mukherji, D., Marques, C. M., Kremer, K. (2017). Collapse in two good solvents, swelling in two poor solvents: defying the laws of polymer solubility? Journal of condensed matter, 024002, 30.

CPP 38.2   Wed 10:00   C 230
Studying Polymer-induced Depletion Effects via Grid-based Simulations — •Qiyun Tang and Marcus Müller — Universität Göttingen, Institute für Theoretische Physik, Friedrich-Hund- Platz 1, 37077 Göttingen, Germany

Recently we found that our modified grid-based coarse-grained simulations could be employed to study the polymer induced depletion effects between nanoparticles in the nanoparticle/protein limit. By analysing the radial distribution function of nanoparticles from simulations, we systematically study the influence of polymer density and also the nanoparticle density on these depletion effects. Results show that in the semidilute region of polymer solution, the contact depletion potential is gradually reduced by increasing nanoparticle's concentration. Similar behavior is also observed in the polymer melt. The simulation results are also compared to the theories, and are consistent with the theoretical prediction in the dilute polymer solutions.

CPP 38.3   Wed 10:15   C 230
Process-directed assembly of copolymer materials — •Marcus Müller — Georg-August-Universität Göttingen, Institut für Theoretische Physik, Göttingen, Germany

Process-directed self-assembly of block copolymers refers to rapid thermodynamic processes that reproducibly direct the kinetics of structure formation from a starting, unstable state into a selected, metastable mesostructure. We investigate the kinetics of self-assembly of linear block copolymers after different rapid changes of thermodynamic control parameters (e.g., photochemical transformations, stretching or mechanical deformation, or pressure changes). These thermodynamic processes convert an initial, equilibrium mesophase of the copolymer material into a well-defined but unstable, starting state. The spontaneous structure formation that ensues from this unstable state becomes trapped in a metastable mesostructure, and we systematically explore, which metastable mesostructures can be fabricated by varying the physical properties of the copolymers in the starting and final state and a step-shear deformation. In addition to the equilibrium mesophases of linear AB diblock copolymers, this diagram of process-accessible states includes multiple, novel, metastable periodic mesostructures; inter alia, Schoen's F-RD periodic minimal surface. Strategies and challenges for studying process-directed self- assembly by particle-based simulations and self-consistent field theory are dis-

cussed and the role of non-equilibrium chain conformations and the diffusive dynamics is highlighted.

CPP 38.4   Wed 10:30   C 230
Non-covalent interactions across organic and biological subsets of chemical space: Physics-based potentials parametrized from machine learning — •Tristan Bereau — Max Planck Institute for Polymer Research, Mainz, Germany

Classical intermolecular potentials typically require an extensive parametrization procedure for any new compound considered. To do away with prior parametrization, we propose a combination of physics-based potentials with machine learning (ML), which is transferable across small neutral organic and biologically-relevant molecules. ML models provide on-the-fly predictions for environment-dependent local atomic properties across conformations and chemical compositions of H, C, N, and O atoms. These parameters enable accurate calculations of intermolecular contributions. Unlike other potentials, this model is transferable in its ability to handle new molecules and conformations without explicit prior parametrization: All local atomic properties are predicted from ML, leaving only eight global parameters—optimized once and for all across compounds. We validate IPML on various gas-phase dimers at and away from equilibrium separation, where we obtain mean absolute errors between 0.4 and 0.7 kcal/mol for several chemically and conformationally diverse datasets representative of non-covalent interactions in biologically-relevant molecules. We further focus on hydrogen-bond complexes—essential but challenging due to their directional nature—where datasets of DNA base pairs and amino acids yield an extremely encouraging 1.4 kcal/mol error.

15 min. break

CPP 38.5   Wed 11:00   C 230
Investigating structural and thermodynamic representability for coarse-grained models of ionic liquids — •Svenja Wörner[1], Joseph Rudzinski[1], Tamisra Pal[2], Michael Vogel[2], Kurt Kremer[1], and Tristan Bereau[1] — [1]Max-Planck-Institut für Polymerforschung, Mainz, Germany. — [2]Technische Universität Darmstadt, Darmstadt, Germany.

Coarse-grained models are usually parameterized to reproduce either structure or thermodynamic properties. The coarse-grained model for the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate developed by Bhargava et al was parameterized to reproduce density and surface tension and therefore lacks detailed structural accuracy. In this work, we investigate to what extent the structural accuracy of this model can be improved while retaining the original thermodynamic target properties. We employ the generalized Yvon-Born-Green framework, which utilizes an integral equation theory that systematically connects the coarse-grained model parameters to the pair correlation functions. This methodology is not only useful for parameterizing new force fields , but can also be used to systematically perturb parts of potentials or to incorporate information from other state points to refine an existing force field. We demonstrate that perturbing only the hard core of the potential of the non-bonded interactions for ionic liquid model significantly improves the structure while retaining thermodynamic information included in the original model. Adding information from multiple temperatures may further improve representablility.

CPP 38.6   Wed 11:15   C 230
Mapping onto ideal chains profoundly overestimates self-entanglements in polymer melts — •Hendrik Meyer[1], Eric Horwath[2], and Peter Virnau[2] — [1]Institut Charles Sadron, CNRS and Université de Strasbourg — [2]Institut f. Physik, Universität Mainz

In polymer physics it is typically assumed that excluded volume interactions are effectively screened in polymer melts. Hence, chains could be described by an effective random walk. In this letter, we show that this mapping is problematic by analyzing the occurrence of knots, their spectrum and sizes in polymer melts, corresponding random walks and chains in dilute solution. The effective random walk severely overrates the occurrence of knots and their complexity, particularly when compared to melts of flexible chains, indicating that non-trivial effects due to remnants of self-avoidance still play a significant role for the chain lengths considered in this numerical study. For melts of semiflexible

chains, the effect is less pronounced. In addition, we find that chains in a melt are very similar in structure and topology to dilute single chains close to the collapse transition, which indicates that the latter are also not well-represented by random walks. We finally show that typical equilibration procedures are well-suited to relax the topology in melts. [1] arXiv:1710.11077

CPP 38.7   Wed 11:30   C 230

Collective dynamics in liquid water: Molecular dynamics simulations — ●Ari Paavo Seitsonen[1] and Taras Bryk[2] — [1]Département de Chimie, Ecole Normale Supérieure, Paris — [2]Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, Lviv

Water, as the most important substance for life, has always attracted the researchers to explore and explain its numerous anomalous properties. Collective dynamics in simple and molecular liquids is so far well understood only on macroscopic length and time scales. Experiments on Brillouin scattering of light on liquids can be described by the hydrodynamic theory, which explains the main relaxation and propagation processes contributing to the scattered intensity of light. Atomistic molecular dynamics simulations is an efficient tool in exploration of the dynamic properties, providing precious information on time-dependent correlations in liquids on nano- and atomic-scale resolution.

Here we report molecular dynamics simulations using density functional theory (DFT), in particular the BLYP approximation to the exchange-correlation term with the augmented D3 empirical term to account for the London dispersion interactions missing in the BLYP. We present results on the collective dynamics [1], and the recently evaluated [2] melting temperature of water using this approach.
[1] Taras Bryk & Ari P Seitsonen Condensed Matter Physics 19 (2016) 23604; DOI: 10.5488/CMP.19.23604

[2] Ari P Seitsonen & Taras Bryk Physical Review B 94 (2016) 184111; DOI: 10.1103/PhysRevB.94.184111

CPP 38.8   Wed 11:45   C 230

Molecular Origin of Urea-driven Hydrophobic Collapse of Polyacrylamides — ●Divya Nayar, Angelina Folberth, and Nico van der Vegt — Technische Universität Darmstadt, Alarich-Weiss-Straße 10, 64287 Darmstadt, Germany

Osmolytes modulate protein folding and affect the water solubility of macromolecules [1]. The osmolyte-induced hydrophobic polymer collapse due to osmolyte depletion from the solvation shell is well-known, however, evidences have indicated direct preferential osmolyte binding that may lead to polymer collapse [2]. To understand the underlying molecular mechanisms better, we examine the role of urea in strengthening and attenuating the hydrophobic collapse of thermo-responsive polyacrylamides i.e. Poly-N-isopropylacrylamide (PNIPAM, secondary amide) and Poly-N,N,-diethylacrylamide (PDEA, tertiary amide) respectively [3]. Using extensive molecular dynamics simulations and large-scale polymer conformational sampling, we show that urea collapses PNIPAM by "preferentially binding" to it. We propose an osmolyte stabilizing mechanism driving PNIPAM collapse, based on the balance in opposing loss of entropic degrees of freedom of urea and water [4]. The study provides new physical insights into the interplay between polymer side-chain chemistry, solvent entropic degrees of freedom and polymer-solvent interactions to understand the osmolyte effects on hydrophobic collapse. [1] D. R. Canchi et al. Annu. Rev. Phys. Chem., 2013, 64, 273. [2] N. F. A. van der Vegt et al. J. Phys. Chem. B 2017, 121, 9986. [3] J. Wang et al. Macromolecules, 2016, 49, 234. [4] D. Nayar et al. Phys. Chem. Chem. Phys. 2017, 19, 18156.